Sulfur Valence-to-Core X-ray Emission Spectroscopy Study of Lithium Sulfur Batteries

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Methods

Preparation of the polysulfide standards and the *ex-situ* samples

The Li_2S_X (X=2, 4, 6, 8) polysulfides and the cathodes used for ex-situ XES measurements were the same as the ones used in our previous work[1] so all details regarding sample preparation can be found there.

XES measurements

The high energy resolution XES measurements were performed at the 2 MV tandem ion accelerator of the J. Stefan Institute in Ljubljana. The x-ray emission was induced by broad unfocused 2 MeV proton beam. Proton induced emission spectra were collected by Johansson-type in-vacuum tender XES spectrometer.[2] Samples were mounted on the motorized sample holder used to exchange targets without breaking the vacuum in the spectrometer chamber. The target holder was tilted at 45° with respect to the incident beam while emission spectra were collected in the direction perpendicular to the incident beam. Emitted photons were reflected in the first order by a Si(111) crystal ($2d$ = 6.271 Å) cylindrically curved with 0.5 m Rowland circle radius. The diffracted photons were recorded by the thermoeletrically cooled (-40°C) charge-coupled device (CCD) camera. In order to achieve dispersive mode of operation and collect simultaneously full VtC spectrum the sample holder was placed inside the Rowland circle at the distance of 42 cm from the crystal. The position spectra recorded by the CCD were converted into energy scale relative to the position of the $K\beta_{1,3}$ emission line of α-S_8 sample with corresponding reference energy of 2467.96[3] eV. The overall acquisition time for a single spectrum was 1.5 - 2.5 hours with the beam current on the sample around 30-50 nA.

Computational methods

Sulfur VtC XES spectra of Li_2S_X polysulfides were obtained from first-principles quantum chemical calculations. Two different program packages based on the density functional theory (DFT)[4] approach were used, StoBe-deMon[5] and CP2K/Quickstep.[6] XES spectra of isolated polysulfide molecules calculated with the StoBe-deMon are continuation of our previous work on XES spectra of third row elements with different oxidation states and local symmetries.[7,8] These calculations have been expanded to take into account also the effects of model solvent, which were calculated with the CP2K program package.

The StoBe-deMon VtC XES calculations of isolated molecules start with the geometry optimization of the polysulfides structure. Here, the TZVP (73111/6111/1) and DZVP (621/1/1)[9] basis set were used for S and Li atoms, respectively. Next, Bader analysis[10] was performed on the ground state electron density in order to calculate partial charges of the atoms (Table S1). The VtC emission spectra were calculated for each S atom within the molecule using optimized coordinates. Here, the (73111/6111/1) basis set was kept only for this particular selected atom, while all other S atoms within the molecule were described by means of an effective core potential in order to avoid linear combination of core-orbitals. Effective electrostatic potential[11] was used for the atomic nuclei and electrons from K and L atomic shells, while the valence electrons were described with (311/211/1) basis set. The VtC x-ray emission spectra were calculated in the ground state approximation. In this procedure the Kohn-Sham orbitals of the ground state are used to represent both the initial core-hole state and the final valence-hole state and the dipole transition moments are calculated as an explicit one-electron transitions.[12,13] The unknown exchange and correlation potentials were substituted by the Becke (Be88)[14] exchange functional and and Perdew (PD91)[15] correlation functional.

Table S1: Average partial charges of sulfur atoms within Li_2S_x polysulfides calculated by Bader analysis.

Li_2S_x	Terminal	Internal	Central
2	-0.943	-	-
3	-0.804	-0.250	-
4	-0.744	-0.185	-
5	-0.729	-0.107	-0.181
6	-0.705	-0.039	-0.181
7	-0.719	-0.029	-0.119
8	-0.705	-0.012	-0.105

The dynamics of the Li_2S_7 molecule within model solvent was calculated with mixed Gaussian and Plane Wave (GPW)[16] code implemented in the CP2K program package. The Perdew-Burke-Ernzerhof (PBE) general gradient approximation[17] was used for the exchange-correlation functional. We have used polarized valence triple-ζ (TZV2P)[18] basis sets with the Goedecker-Teter-Hutter (GTH) pseudopotentials.[19] We have also taken into account

DFTD3 semi-empirical dispersion corrections of Grimme et al.[20] The cutoff was determined by multiplying relative cutoff value with the largest exponent in the basis set, where relative cutoff value were 40 and 50 Ry for NVT and NPT ensemble, respectively. First, the structure of isolated molecules (Li_2S_7, DOL, LiTDI) were obtained by geometry optimization. The optimized structures were inserted in a box and two models solvent were built. In the first model the Li_2S_7 molecule was surrounded with six DOL molecules and in the second model with five DOL molecules and one LiTDI molecule, similar models were used in work of Liu et al.[21] In order to equilibrate the systems, Langevin dynamics with $\gamma = 0.01\ fs^{-1}$ was performed for first 5 *ps* and final coordinates were used as an input for additional 10 *ps* of NPT dynamics (isobaric-isothermal ensembles). Atomic coordinates of the closest average of the last 5 *ps* of NPT-AIMD were then selected as an input for 21 *ps* NVT (canonic ensemble) simulation. The dynamics was explored at 1 *bar* and 300 *K*, with the Nos-Hoover chain algorithm.[22] Hydrogen masses were increased to tritium which allowed us to use 1 *fs* time step in all simulations.[23] The example of the AIMD CP2K code can be found in Listing 1.

Atomic coordinates of the NVT dynamics from every 3 ps were selected as an input for VtC XES calculations. All-electrons approach based on the Gaussian and Augmented Plane Wave (GAPW)[24] was applied, which allowed us to use the same formalism as in the StoBe program package. The S VtC XES spectra were obtained from frozen-ground state orbitals, where explicit dipole transition moment integrals were calculated for transitions between S 1s core orbital and the valence orbitals.[25,26] The polarization consistent basis (pc-3)[27] basis set was used for the selected sulfur atom within polysulfide molecule.

The theoretical Kβ XES spectra were built from the corresponding stick spectra calculated with both codes (StoBe and CP2K) broadened by the natural linewidth due to core-hole lifetime and the experimental resolution of the spectrometer. For that purpose Voigt profiles were used, the final widths of 0.61 eV and 0.57 eV for the Lorentzian and Gaussian components, respectively were obtained by fitting the broadened α-S theoretical spectrum to the measured spectrum. In order to match absolute experimental emission energies an overall shifts of the energy scale of 75.42 eV and 77.47 eV were applied to the theoretical spectrum of the α-S calculated by Stobe and CP2K, respectively. These parameters were than applied to calculated stick spectra of all lithium polysulfides. For each isolated polysulfide molecule the final S VtC XES spectra calculated by StoBe and CP2K match each other well. The Visual Molecular Dynamics (VMD)[28] program package was used to evaluate the radial distribution functions from AIMD simulations. The Python based Lmfit package[29] was used in fitting procedure.

Theoretical VtC XES spectra of isolated molecules

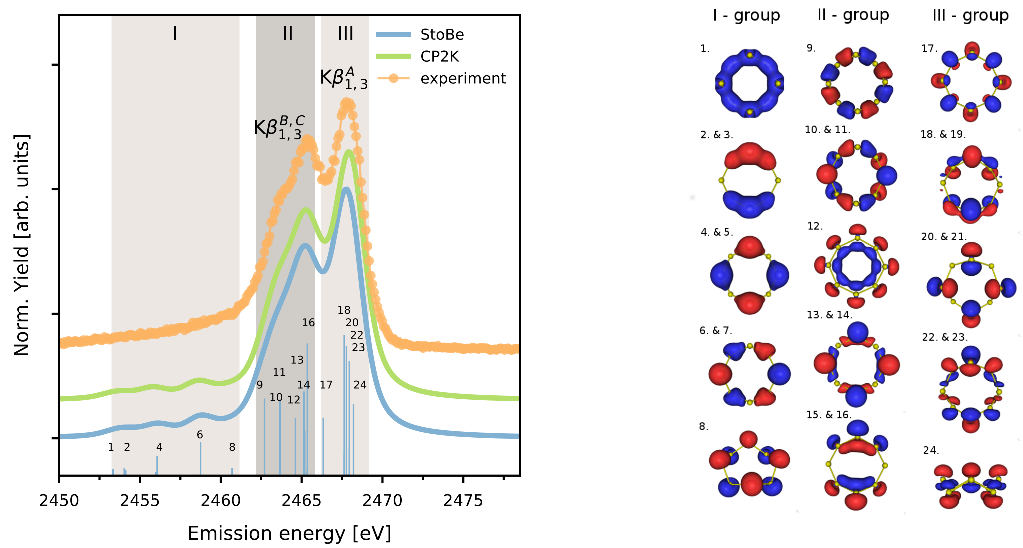

Figure S1: *(left)* Comparison of the experimental and theoretical S Kβ x-ray emission spectrum of α-S_8. The theoretical calculations were done with StoBe-deMon and CP2K program packages for the single isolated molecule. *(right)* Electron density isosurfaces for corresponding valence orbitals of α-S_8 calculated on the ground state of the molecule.

Since elemental sulfur α-S_8 is a chemically stable compound clean experimental VtC XES spectrum can be obtained and compared directly to the theoretical model. The experimental and the theoretical VtC x-ray emission spectrum of α-S_8 are presented in Figure S1. The experimental spectrum is characterized by two close-lying components, commonly labeled

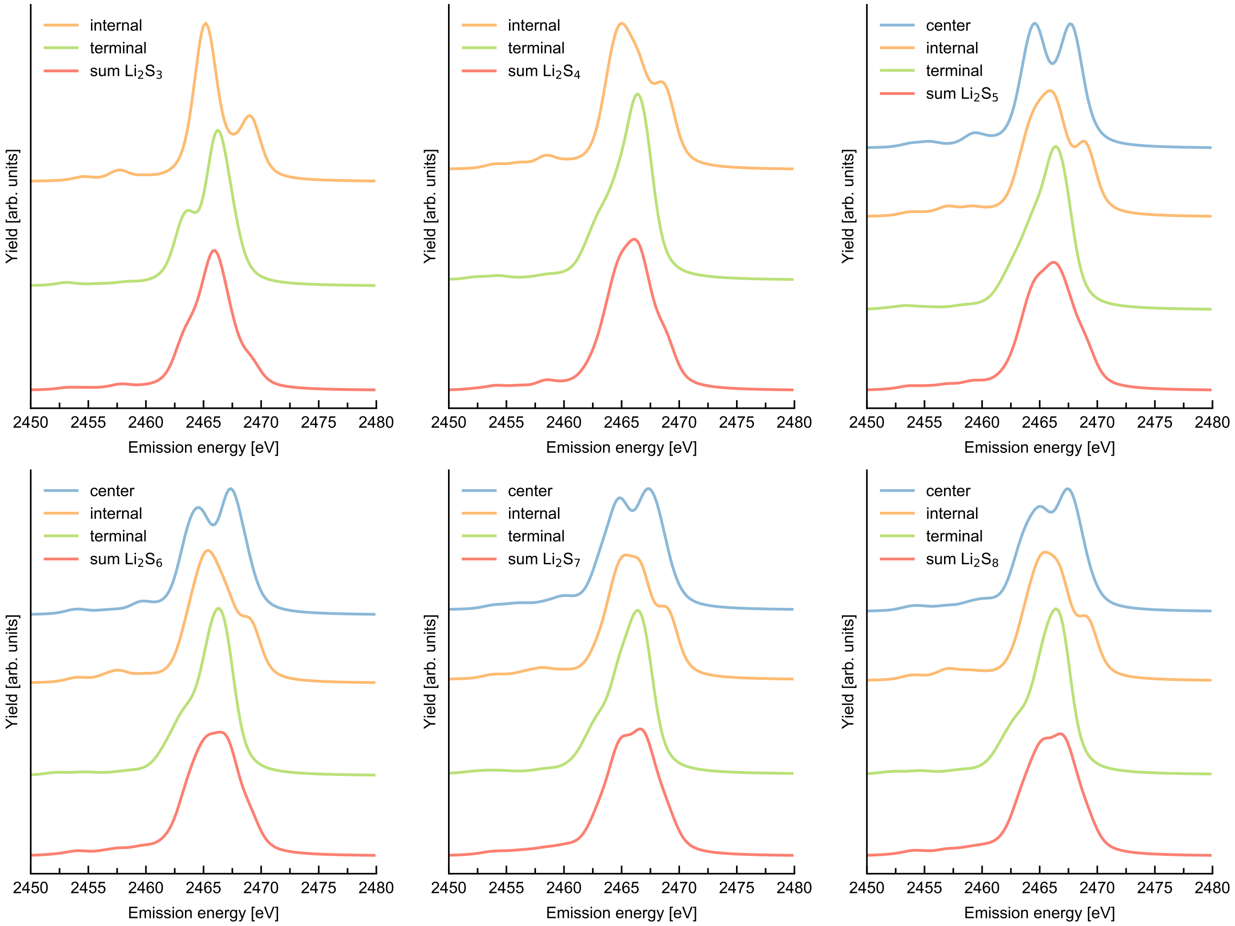

Figure S2: Theoretical sulfur VtC XES spectra of lithium polysulfides (red), constructed by summing up the calculated spectra from corresponding central (blue), internal (orange), and terminal (green) sulfur atoms.

as $\mathrm{K}\beta_{1,3}^{A}$ and $\mathrm{K}\beta_{1,3}^{B,C}$. The theoretical spectrum was built from the calculated stick spectrum which is also presented in Figure S1 and labeled by numbers. The labels correspond to the valence molecular orbitals being involved in radiative electron dipole transitions to the atomic like $1s$ orbital. Valence molecular orbitals building the α-S VtC XES spectrum can be classified into three distinct groups (Figure S1, right). Molecular orbitals in the first group are primarily built from atomic orbitals with s-character and can therefore not participate in the dipole transitions to the $1s$ orbital. Their minor contribution to the calculated spectrum is due to small amount of the atomic orbitals with p-character. Molecular orbitals from second and third groups are predominantly composed of sulfur $3p$ orbitals contributing to the $\mathrm{K}\beta_{1,3}^{B,C}$ and $\mathrm{K}\beta_{1,3}^{A}$ peaks, respectively. The separation of these two peaks can be understood by looking into the arrangement of corresponding electron density. The electron density in the orbitals from the second group is arranged between sulfur atoms and these can be characterized as p-bonding orbitals. On the other hand, the electron density in the orbitals from the third group is located mostly on the sulfur atoms with nodes of the wavefunctions between them. The third group of orbitals can be therefore characterized as p-antibonding orbitals.

An excellent agreement between experimental and calculated α-S_8 VtC XES spectrum serves us to validate the theoretical approach, which is used to calculate emission spectra of Li_2S_X polysulfides. The final theoretical spectra of the lithium polysulfides are presented in Figure S2.

Besides the same overall alignment of calculated spectra used to match the experimental XES energies no additional relative alignment was applied to the spectra of different molecular species. This is consistent with the previous work,[12] showing that for XES calculations transition moments from ground state orbitals give good agreement with the experiment. In order to confirm this also for our specific case, we have additionally calculated the emission energies as the differences of relaxed core hole and valence hole state for the Li_2S_3 molecule (ΔKS approach). The relative alignment between calculated XES contributions from differ-

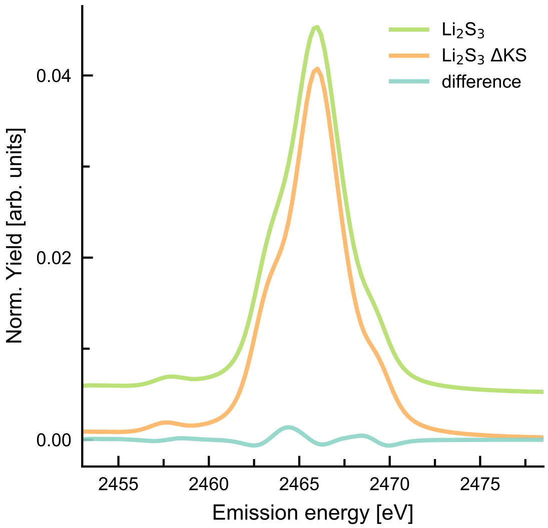

Figure S3: Comparison between VtC emission spectra calculated on the ground state orbitals (green) and with ΔKS approach (orange) for the Li$_2$S$_3$ molecule.

ent S atoms (terminal/internal/central) is preserved and the calculated spectral shape is the same proving that one-electron DFT-GGA formalism is sufficient in our case (Fig. S3).

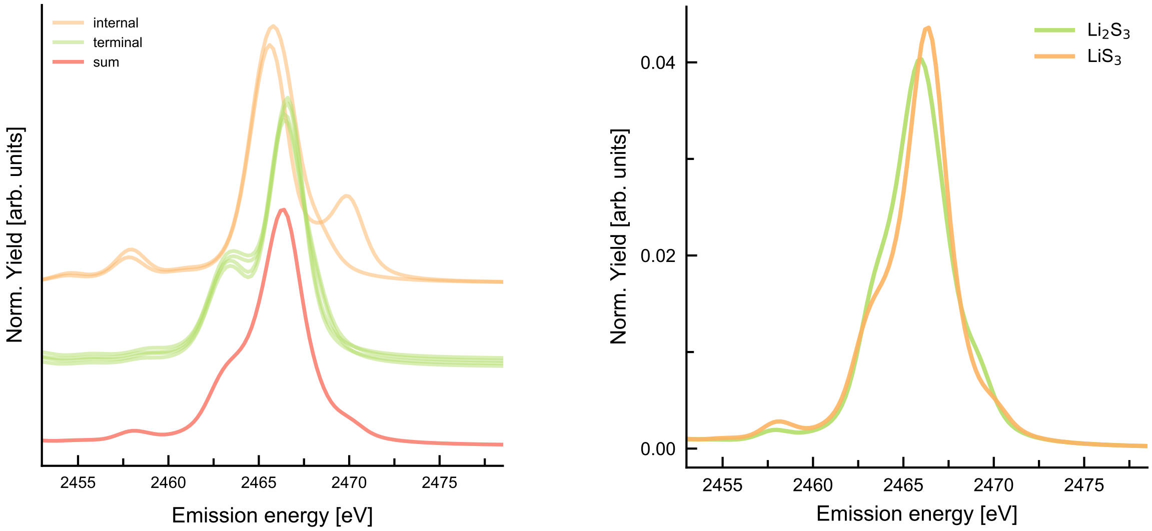

Figure S4: Theoretical VtC XES spectra calculated for LiS$_3$ radical *(left)* and compared with the theoretical spectra of Li$_2$S$_3$ molecule *(right)*

Besides polysulfides the reduction of sulfur within the battery cathode can produce also polysulfide radicals.[30,31] In order to clarify the spectral contributions of radicals to the reported XES spectra we have performed additional calculations for LiS$_3$ radical. The spectra for each separate sulfur atom and for both spin configurations are presented in Figure S4 together with the comparison between theoretical VtC XES spectra of Li_2S_3 and LiS_3 complexes. For one of both spin configurations in internal S atom the high energy component corresponding to the transition from singly-occupied molecular orbital (SOMO) is absent resulting in small difference between the spectra of radical and corresponding polysulfide. This difference is not significant enough that we could evidence radical formation in our experimental XES spectra so we have restricted our discussion to polysulfide molecules.

AIMD calculations

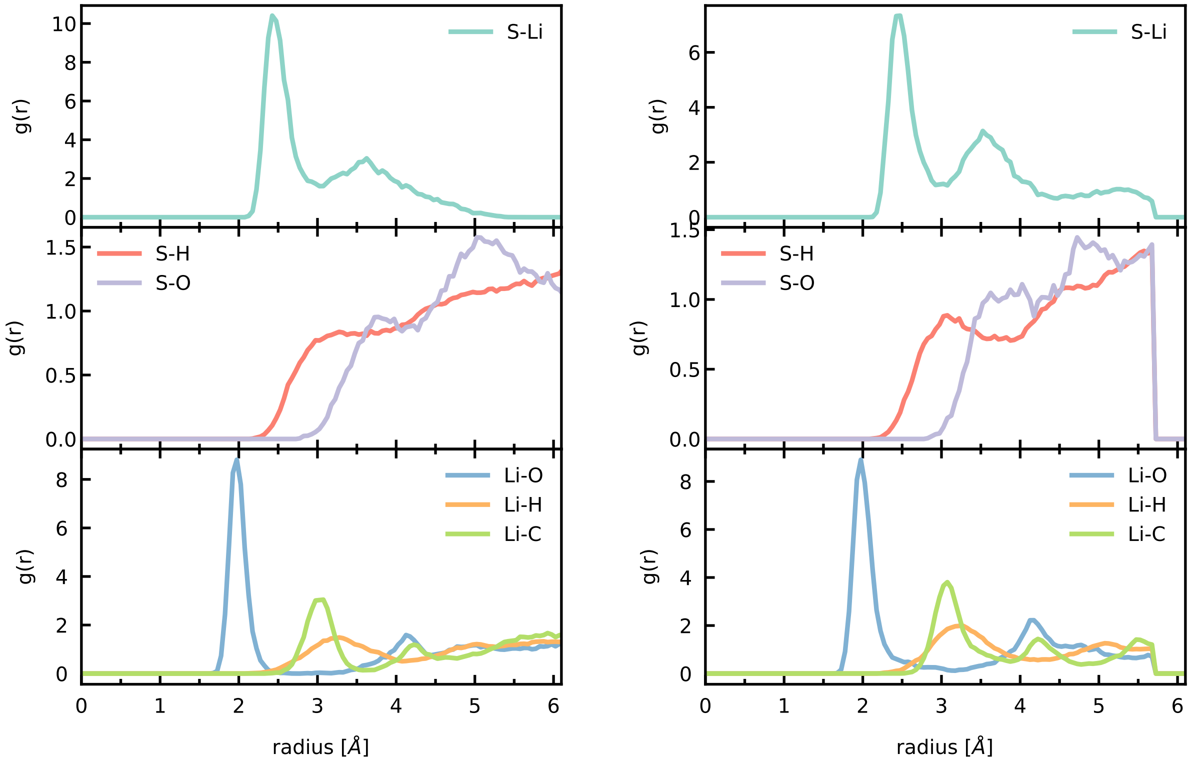

Figure S5: *(left)* Calculated radial distribution functions for Li_2S_7 molecule in model solvent composed of six DOL molecules *(right)* and the second solvent composed of five DOL molecules and one LiTDI molecule.

In order to calculate also XES spectra of dissolved polysulfides ab-initio molecular dynamics (AIMD) calculations for Li_2S_7 in two model solvents were performed. The radial distribution functions calculated for Li_2S_7 in both model solvents are presented in Figure S5. For first model solvent composed of six DOL molecules a good agreement was found with the work of Kamphaus and Balbuena.[23]

The distance between sulfur atoms in S-S bonds within Li_2S_7 were evaluated from NVT molecular dynamics calculations (21000 snapshots). In the first model solvent with six DOL molecules an average distance between central sulfur atoms was found 2.1467(7) Å, between central-internal atoms 2.0963(5) Å and between internal-terminal atoms 2.0875(3) Å, respectively. This is in good agreement with the work of Liu et al.[21] For each Li atom the average distance from both terminal S atoms were found 2.461(1) Å and 2.577(1) Å. In case of second model solvent with one LiTDI molecule the average distance between central sulfur atoms was found 2.956(7) Å. The distances between central-internal and internal-terminal atoms were found 2.0873(6) Å and 2.0573(3) Å, respectively. The average distance between the third Li atom and two nearest central S atoms was found 3.342(3) Å.

Finally, the VtC XES spectra of Li_2S_7 in both model solvents were calculated after 15 ps AIMD simulation and the results are presented in Figure S6 together with the spectrum of isolated molecule.

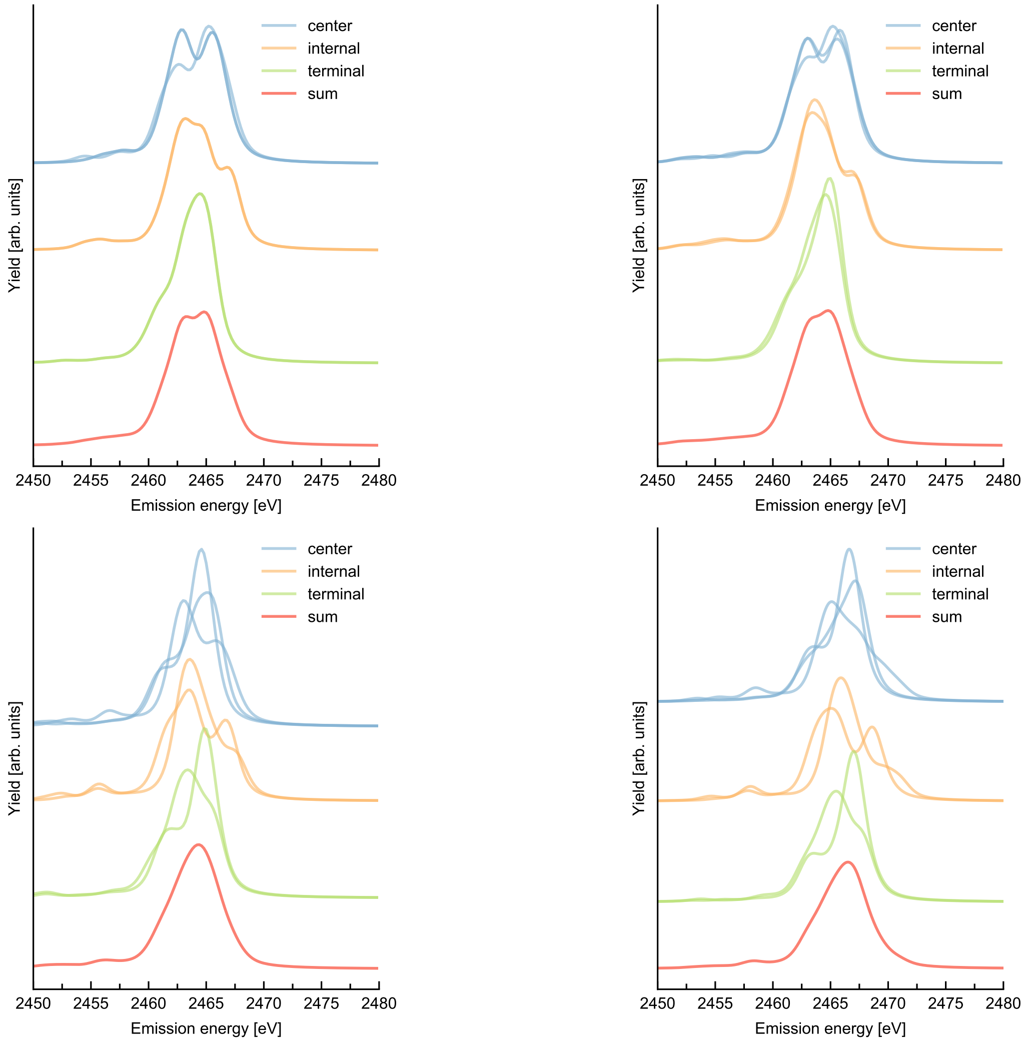

Figure S6: Theoretical VtC XES spectra calculated for each sulfur atom within isolated Li_2S_7 molecule *(top-left)*, Li_2S_7 surrounded with either six DOL molecules *(top-right)* or five DOL and one LiTDI molecule *(bottom-left)*, both calculated after 15 ps AIMD simulation. XES spectrum for Li_2S_7 in second model solvent calculated after 15 ps AIMD simulation, with all remaining atoms besides seven S and three Li removed from the system *(bottom-right)* .

References

(1) Kavčič, M.; Petric, M.; Rajh, A.; Isaković, K.; Vizintin, A.; Talian, S. D.; Dominko, R. *submitted to ACS Appl. Energy Mater.*

(2) Kavčič, M.; Budnar, M.; Mühleisen, A.; Gasser, F.; Žitnik, M.; Bučar, K.; Bohinc, R. *Rev. Sci. Instum.* **2012**, *83*, 03311.

(3) Kavčič, M.; Dousse, J.-C.; Szlachetko, J.; Cao, W. *Nucl. Instrum. Methods Phys. Res. B* **2007**, *260*, 642 – 646.

(4) Kohn, W. *Rev. Mod. Phys.* **1999**, *71*, 1253–1266.

(5) Hermann, K. et al. 2011; `http://www.fhi-berlin.mpg.de/KHsoftware/StoBe/index.html`.

(6) Khne, T. D. et al. *J. Chem. Phys.* **2020**, *152*, 194103.

(7) Petric, M.; Bohinc, R.; Bučar, K.; Nowak, S. H.; Žitnik, M.; Kavčič, M. *Inorg. Chem.* **2016**, *55*, 5328–5336.

(8) Petric, M.; Kavčič, M. *J. Anal. At. Spectrom.* **2016**, *31*, 450–457.

(9) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560–571.

(10) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893–928.

(11) Pettersson, L. G. M.; Wahlgren, U.; Gropen, O. *J Chem. Phys.* **1987**, *86*, 2176–2184.

(12) Nilsson, A.; Pettersson, L. G. M. *Surf. Sci. Rep.* **2004**, *55*, 49–167.

(13) Triguero, L.; Pettersson, L. G. M.; Ågren, H. *J. Phys. Chem. A* **1998**, *102*, 10599–10607.

(14) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098–3100.

(15) Perdew, J.; Chevary, J.; Vosko, S.; Jackson, K.; Pederson, M.; Singh, D.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671–6687.

(16) Lippert, G.; Hutter, J.; Parrinello, M. *Mol. Phys.* **1997**, *92*, 477–488.

(17) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.

(18) VandeVondele, J.; Hutter, J. *J. Chem. Phys.* **2007**, *127*, 114105.

(19) Goedecker, S.; Teter, M.; Hutter, J. *Phys. Rev. B* **1996**, *54*, 1703–1710.

(20) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(21) Liu, Q.; Mu, D.; Wu, B.; Wang, L.; Gai, L.; Wu, F. *RSC Adv.* **2017**, *7*, 33373–33377.

(22) Martyna, G. J.; Tobias, D. J.; Klein, M. L. *J. Chem. Phys.* **1994**, *101*, 4177–4189.

(23) Kamphaus, E. P.; Balbuena, P. B. *J. Phys. Chem. C* **2017**, *121*, 21105–21117.

(24) Lippert, G.; Hutter, J.; Parrinello, M. *Theor. Chem. Acc.* **1999**, *103*, 124–140.

(25) Iannuzzi, M.; Hutter, J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1599–1610.

(26) Iannuzzi, M. *J. Chem. Phys.* **2008**, *128*, 204506.

(27) Jensen, F.; Helgaker, T. *J. Chem Phys.* **2004**, *121*, 3463–3470.

(28) Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graph.* **1996**, *14*, 33 – 38.

(29) Newville, M.; Stensitzki, T.; Allen, D. B.; Ingargiola, A. LMFIT: Non-Linear Least-Square Minimization and Curve-Fitting for Python. **2014**, DOI: `10.5281/zenodo.11813`.

(30) Wujcik, K. H.; Pascal, T. A.; Pemmaraju, C. D.; Devaux, D.; Stolte, W. C.; Balsara, N. P.; Prendergast, D. *Adv. Energy Mater.* **2015**, *5*, 1500285.

(31) Wang, Q.; Zheng, J.; Walter, E.; Pan, H.; Lv, D.; Zuo, P.; Chen, H.; Deng, Z. D.; Liaw, B. Y.; Yu, X.; Yang, X.; Zhang, J.-G.; Liu, J.; Xiao, J. *J. Electrochem. Soc.* **2015**, *162*, A474–A478, DOI: `10.1149/2.0851503jes`.

Listing 1: The CP2K example code

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    STEPS    21000
    TEMPERATURE 300
!    &BAROSTAT
!      TIMECON [fs] 100
!      PRESSURE [bar] 1.0
!    &END BAROSTAT
    &THERMOSTAT
      REGION GLOBAL
      TYPE NOSE
      &NOSE
        TIMECON [fs] 10.
      &END
    &END THERMOSTAT
  &END MD

  &PRINT
...
  &END PRINT
&END MOTION

&FORCE_EVAL
```

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  POTENTIAL_FILE_NAME  POTENTIAL

  &QS
     METHOD GPW
     EPS_DEFAULT 1.0E-12
     EXTRAPOLATION ASPC
     EXTRAPOLATION_ORDER 5
  &END

  &MGRID
    NGRIDS 4
    CUTOFF 420   !! 550
    REL_CUTOFF 40  !! 50
  &END MGRID

  &SCF
    SCF_GUESS ATOMIC
    MAX_SCF 25
    EPS_SCF 1.0E-6
    &OT
      PRECONDITIONER FULL_ALL
      MINIMIZER DIIS
    &END OT
    &OUTER_SCF
      MAX_SCF 5
      EPS_SCF 1.0E-6
    &END OUTER_SCF
    &PRINT
```

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        &END
      &END
    &END SCF

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      &END XC_FUNCTIONAL
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         POTENTIAL_TYPE PAIR_POTENTIAL
         &PAIR_POTENTIAL
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            TYPE DFTD3
            REFERENCE_FUNCTIONAL PBE
            R_CUTOFF [angstrom] 15
         &END
      &END VDW_POTENTIAL
    &END XC

    &POISSON
       PERIODIC XYZ
    &END
  &END DFT

  &SUBSYS
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      ABC 8.75668 9.710337 10.83691
!!      &CELL_REF
!!        ABC 12.0 12.0 13.0
!!      &END
    &END CELL
    &TOPOLOGY
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    &END

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      ELEMENT C
      BASIS_SET TZV2P-GTH-q4
     POTENTIAL GTH-PBE-q4
    &END KIND
    &KIND O
      ELEMENT O
      BASIS_SET TZV2P-GTH-q6
      POTENTIAL GTH-PBE-q6
    &END KIND
    &KIND H
      ELEMENT H
      MASS 3.0160
      BASIS_SET TZV2P-GTH-q1
      POTENTIAL GTH-PBE-q1
    &END KIND
    &KIND S
      ELEMENT S
      BASIS_SET TZV2P-GTH-q6
     POTENTIAL GTH-PBE-q6
    &END KIND
    &KIND Li
      ELEMENT Li
      BASIS_SET TZV2P-GTH-q3
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    &END KIND
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&END FORCE_EVAL
```